BEHAVIOR OF IRON BEARING MINERALS IN THE EARLY STAGES OF PULVERIZED COAL CONVERSION PROCESSES

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ABSTRACT

Early stage transformations and deposition of iron bearing coal minerals, in particular pyrite (FeS_2) were studied. An atmospheric lab-scale facility was used to simulate the near burner environments in two different coal conversion processes: i) Low-NO_x pulverized fuel combustion and ii) Entrained-flow gasification. Particle sampling showed that for both environments, the pyrite was transformed quickly to pyrrhotite (FeS). In the deposition experiments this pyrrhotite impacts on the substrates.
In the deposition experiments, the chemical composition and the morphology of the slags formed under the two conditions showed clear differences. Special attention was payed to the role of sulphur. Based on these (preliminary) experiments, a mechanistic model is proposed for the transformations of pyrite in both pulverized coal conversion systems. Furthermore a description is given of a new experimental setup for future work at elevated pressures (up to 20 bar) to enable a closer simulation of pressurized entrained-flow coal gasification processes.

INTRODUCTION

In the Netherlands, oxygen-blown entrained-flow gasification has been selected as the most promising technology for large scale coal-based power generation. This is mainly due to its fuel flexibility, high efficiency and relatively low environmental impact. The world's first fully integrated Gasification Combined Cycle (IGCC) demonstration plant (250 MWe) based on (Shell) gasification technology is currently in operation in Buggenum.

To support and ensure a successful introduction of IGCC and other new coal-based power generation technologies, the coal-related research at ECN is extended to include these technologies. To this purpose, the staged flat flame burner concept has been adapted which was successfully applied earlier to simulate (low-NO_x) pulverized coal combustion conditions accurately on a laboratory scale (1,2). The atmospheric test facility was reconstructed from an open up-fired to a closed down-fired system, where the off-gases are flared. The facility was renamed as the Atmospheric Entrained-Flow Gasification and Combustion simulator (AEFGC-simulator). The coal/mineral particles are carried along in the combustion gas and thus the high initial temperatures and very rapid particle heat-up in both combustion and gasification can be simulated in this facility.

For entrained-flow gasification conditions, the mechanism of the formation of slags was explored by depositing the mineral particles onto alumina plates, simulating gasifier wall. The plates were held at a temperature of around 1450 °C, characteristic for that of the wall in an actual entrained-flow gasifier (3). Experience with slag production in the reducing environment of low-NOx burners (4,5) was used in the evaluation of the results.

EXPERIMENTAL

Laboratory-scale test facility

The test facility is an entrained-flow reactor with an integrated, premixed and multistage flat flame gas burner. A schematic view of the simulator is given in Figure 1. The burner consists of two sub-burners viz. an inner burner (10.9 mm) and an outer burner (60.7 mm). A tertiary gas stream (consisting of nitrogen) is applied to create suitable mixing profiles and to protect the tube from the hot secondary gas stream. Coal/char particles are fed through the inner burner and undergo rapid heating (> 10^5 °C/s) up to the high temperature level of the near-burner zone in the actual process. The particles are fed at a feed rate of approximately 1 g/h by means of a rotating brush feeder (4). The gas/particle flow is confined to a 76 mm ID (ceramic) reactor tube with a length of 550 mm. The tube is surrounded by a controllable heating section equipped with Kanthal Super 33 elements to create the required temperature history for the particles.

Coal choice

The experimental work has been performed with pyrite rich coal (Prince coal, Canada). Coal with a high content of iron minerals (pyrite) was chosen because iron is known to react with the reducing gasifier gas. Narrow size fractions (pyrite enriched) were used in the experiments. The specifications of this coal and preparation techniques have been described in detail elsewhere (4).

Sampling and analysis

Sampling of in-flame particles was carried out with a quench probe followed by a cyclone and a filter. Ash particles were sampled isokinetically from the hot gas at distances corresponding to residence times of 90, 120, 170 ms using a helium-fed quench probe under entrained-flow gasification conditions. However, for combustion conditions, ash particles were sampled at distances corresponding to residence times of 18, 22, 50 and 120 ms. Experimental conditions used in the present investigations are given in Tables 1 and 2. The samples were analyzed with SEM with simultaneous characterization of composition and morphology. In addition, a deposition probe was used for slagging tests. On this probe different substrate materials (high grade Al_2O_3 and SiC) were placed to simulate wall surface material. The plates were placed at distances corresponding to residence times of 50ms for combustion conditions and 90, 120, 170ms for gasification conditions. The plates were held in the particle stream for 15 minutes at a furnace wall temperature of 1500 °C. After completion of the test, cold helium gas was introduced along the plates via the tip of the probe holder. Perpendicular cross-sections through the deposit plates and attached deposits were examined with SEM for internal structure. Single spots and complete layers were analyzed. Elemental mapping was also performed to obtain the profile for a given element in the layer. The measured gas temperatures for both low-NO_x combustion and entrained-flow gasification conditions are as shown in Figure 2.

RESULTS

Both the results obtained for low-NO_x combustion and entrained-flow gasification conditions are detailed in the following sections.

Ash formation experiments

Analysis of ash particles formed under entrained-flow gasification revealed the formation of cenospheres, clusters (50-60 µm) and some skeletal structures. Several small fragments were also found which consisted of Al, Si, Fe and K. Similar ash particles were formed under low-NO_x combustion conditions.

Figure 3 summarizes the measured sulphur to iron ratios both under simulated low NO_x conditions, as extracted from earlier work (5), and simulated entrained-flow gasification conditions. The measured ratio of S/Fe present as pyrite in the coal is shown in the figure for comparison purposes. From the figure it can be observed that for combustion conditions the pyrite transforms quickly to pyrrhotite (FeS) in 20 ms. At increasing residence times a further transformation to FeOS or FeO found to occur. For entrained-flow gasification, also a quick transformation to pyrrhotite occurs. However, here the pyrrhotite appears to be remain stable at longer residence times. Nevertheless, it should be noted that the gasification experiments were conducted with 1% H_2S in the gas, while no sulphur compound was added in the combustion experiments.

Deposition experiments

Low-NO_x combustion

Figure 4 shows the internal structure of the deposit. Elemental analysis closer to the plate showed enrichment in Al. This strongly suggests interaction of slag with substrate material (Alsint). The crystals at the top and bottom are spinels (iron-alumina). These deposits consisted of several dendrites enriched in iron were found (Figure 4). The iron enrichment in the top and first layer is presumably due to preferential crystallization of iron-alumina spinel at these regions. The slag matrix (second layer) was enriched in silicon. Analysis of the deposits showed no sulphur.

Entrained-flow gasification

Figure 5 shows the cross-sectional view of the deposit plate and the deposits collected at three locations within the reactor. All the deposits contained several bubbly regions. Slag flow was observed for the deposits collected at two locations (viz. 270 mm, 370 mm) within the reactor. However, for the deposits collected at a distance of 520mm, no slag flow was observed along the sides of the deposit plate. This is probably due to misalignment of the probe within the reactor. In addition, changing gas environments may have led to this sort of slag flow behavior. This requires further attention. The slag matrix in all deposits was rich in Fe, Si, Al and small proportions of O. Also some interaction of iron with SiC substrate material was seen. Especially the analysis of the white spots (see Figure 5a) at the interface revealed Fe and Si. No sulphur was found in the deposits.

MECHANISTIC MODEL FOR PYRITE TRANSFORMATIONS

Observed flame transitions of pyrite under low NO_x combustion and entrained-flow gasification conditions are shown in Figure 6. It appears from the experimental results that the first reaction process is not oxidation but decomposition of pyrite into pyrrhotite in both processes (see Figure 3). This may be explained by the evolution of sulphur gas which prevents the oxygen from reaching the particles (6). The rapid melting of the pyrrhotite was evidenced by the rounded shape of the collected particles. Overall, the present test results indicate that the final product for low NO_x combustion being Fe_2O_3 whereas for entrained-flow gasification Fe is the final product.

Although our preliminary experiments have shown that both combustion and gasification processes can be realized in the AEFGC-simulator, it would be more appropriate to conduct the gasification tests at elevated pressures. To enable these experiments at elevated pressures (up to 20 bar), new experimental facility based on the same concept has been built (the so-called Pressurized Entrained-Flow Gasification simulator). Commissioning work of this facility is currently in progress and it will be available for carrying out experiments at elevated pressures early 1996.

CONCLUSIONS

Preliminary experiments have shown that both the low-NO_x combustion and entrained-flow gasification experiments can be realized in the AEFGC-simulator. Irrespective of the gas conditions prevailing within the reactor, the deposits did not contain sulphur. Ash particles collected in the vicinity of the burner before deposition showed sulphur in the sample, suggesting the transformation of pyrite to pyrrhotite. Upon deposition the sulphur in pyrrhotite appeared to be released from the slag into the gas phase. End products in the slag for both low NO_x combustion and entrained-flow gasification processes were determined to be Fe_2O_3 and Fe respectively.

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REFERENCES

[1] H.M. ten Brink, S. Eenkhoorn and G. Hamburg: *Slagging in entrained-flow gasification and low-NO_x firing conditions.* In: Proc. Engineering Foundation Conference on 'The Impact of Ash Deposition on Coal Fired Plants', June 20-25, 1993, Solihull, U.K. (ed. Williamson, J. and Wigley, F., UK, 1994), pp 113-122.

[2] H.M. ten Brink, S. Eenkhoorn and M. Weeda: *Flame transformations of coal-siderite*. In: Proc. Engineering Foundation Conference on 'The Impact of Ash Deposition on Coal Fired Plants', June 20-25, 1993, Solihull, U.K. (ed. Williamson, J. and Wigley, F., UK, 1994), pp 373-383.

[3] R. Wetzel: *PRENFLO-Pressurized Entrained-Flow Coal Gasification. Final Report Phase 2*, Report EUR 13091 EN, 1990.

[4] H.M. ten Brink, S. Eenkhoorn and G. Hamburg: *Flame-transformations of coal-pyrite*, ECN-report ECN-RX--95-037 [1995]. Also submitted to Fuel (July, 1995).

[5] H.M. ten Brink, S. Eenkhoorn and G. Hamburg: *A mechanistic study of the slag formation from iron-rich coals*, ECN-report ECN-RX--95-041 [1995]. Also submitted to Fuel Processing Technology (August, 1995).

[6] Srinivasachar, S. and A.A. Boni: *A kinetic model for pyrite transformations in a combustion environment*, Fuel 1989, 68, 29.

Table 1: Gas mixtures before combustion (gas flows in ln/min)

	Low-NO_x combustion		Entrained-flow gasification	
	Inner Burner	Outer burner	Inner Burner	Outer burner
CH_4	0.133	3.98	0.5	0.2
CO				15
CO_2			1.56	
O_2			1	1.67
H_2S			0.008	
Air	1.0	30.0		

Table 2: Experimental conditions

	Low-NO_x combustion	Entrained-flow gasification
Particle feed rate (in g/h)	1	1
Furnace temperature (°C)	1500	1450
Sampling residence times (ms) sample 1 sample 2 sample 3 sample 4	 18 22 50 120	 90 120 170 -
Deposit substrate	High grade Al_2O_3	High grade SiC
Deposit plate	15mm x 50mm, 2mm thick	15mm x 50mm, 2mm thick
Deposit formation time (min)	15	20

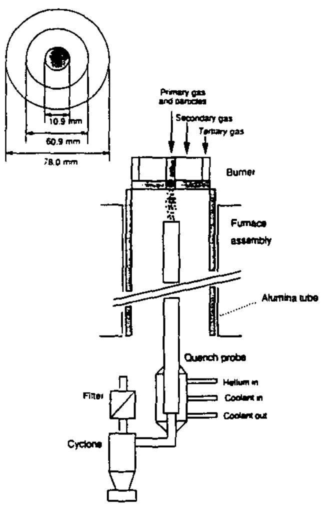

Figure 1: Atmospheric Entrained-Flow Gasification and Combustion simulator (AEFGC-simulator).

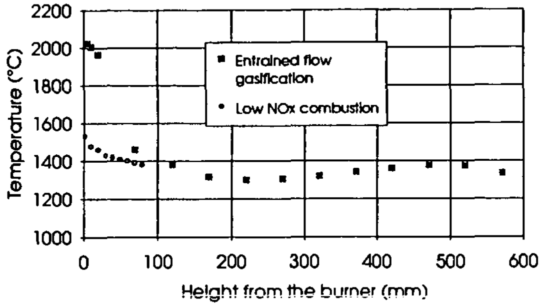

Figure 2: Measured gas temperature profiles within the reactor.

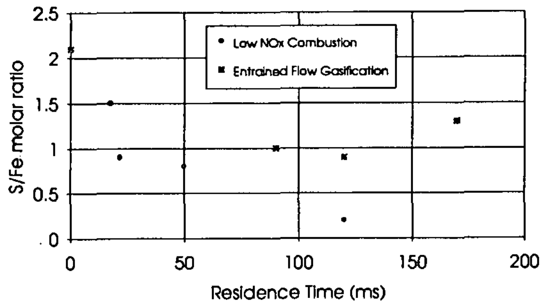

Figure 3: Sulfur to iron molar ratio against reaction time.

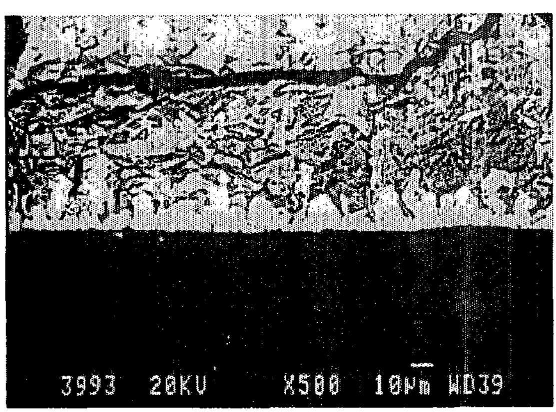

Figure 4: Cross-section perpendicular through the deposit plate (combustion experiments)

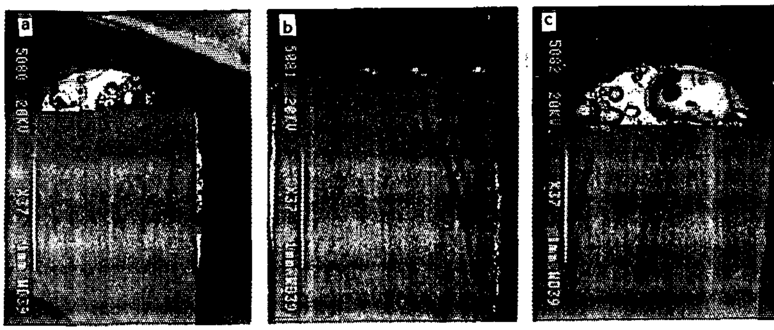

Figure 5: Cross-section perpendicular through the deposit plate (gasification experiments) at different probe locations. a) 270mm; b) 370mm; c) 520mm.

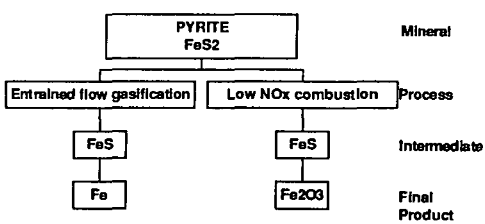

Figure 6: Mechanistic model for pyrite transformations